Conversion of Polyethylene Waste Plastic to Syngas with a Chemical Looping Approach

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Abstract

Large-scale plastic disposal has become an increasing environmental threat, and current recycling methods of the material are relatively inefficient and underused. Thus, an effective conversion of waste plastic to useful products must be discovered. This project seeks to utilize chemical looping technologies to efficiently recycle polyethylene, one of the main components of plastic waste. Specifically, high density polyethylene (HDPE) pellets are examined as a chemical looping reactor feedstock. HDPE pellets are converted into a gaseous mixture of high purity hydrogen and carbon monoxide, which is known as synthesis gas (syngas), in a co-current, moving bed reactor. Based on the ratio of hydrogen to carbon monoxide in the syngas, specific fuel products can be made. This project seeks a hydrogen to carbon monoxide ratio of two, which is ideal for synthesizing methanol. The syngas is formed by partially oxidizing the HDPE pellets with metal composite oxygen carriers, which also form small amounts of other gaseous byproducts. Initially, the reactor setup was modelled using Aspen Plus simulation software, in which a series of sensitivity analyses were performed to determine optimal reactor operating conditions. Next, bench-scale testing of the recycling process took place in a moving bed reducer chemical looping system, in order to determine the efficacy of polyethylene to syngas conversion. HDPE was found to be a promising carbonaceous feedstock in the chemical looping process, achieving a near ideal hydrogen to carbon monoxide ratio with high syngas purity and few operational issues.

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1.1 Waste Plastic Issue

The continually growing production and disposal of plastic products is one of the leading global environmental issues, littering the oceans and landfills all over the world. Due to the stable structure of plastics, their existence in nature is accumulating rather than decomposing, causing a massive buildup of waste plastic in oceans and landfills all over the world. Besides merely being an eyesore, waste plastic causes immense damage to marine ecosystems through ingestion, trapping, and microplastic poisoning[1]. There is also a potential that as marine life ingests harmful microplastics, they could eventually be consumed by humans as the food chain progresses, which could adversely affect human health[1]. Additionally, waste plastics remove valuable fossil fuels from the earth, have relatively short product lifetimes, and very few plastic products are recycled into new products. This is in part due to the fact that many forms of plastic do not have any existing large-scale recycling processes[2]. In fact, from 1950 (when plastic production was first being commercialized) to 2015, only around 9% of cumulative waste plastic has been recycled, while 12% has been incinerated, and the rest has simply been discarded[3]. This is based off a total waste plastic production of 6300 Mt. The overall life cycles of plastic manufacturing from 1950 to 2015 is depicted in Figure 1.

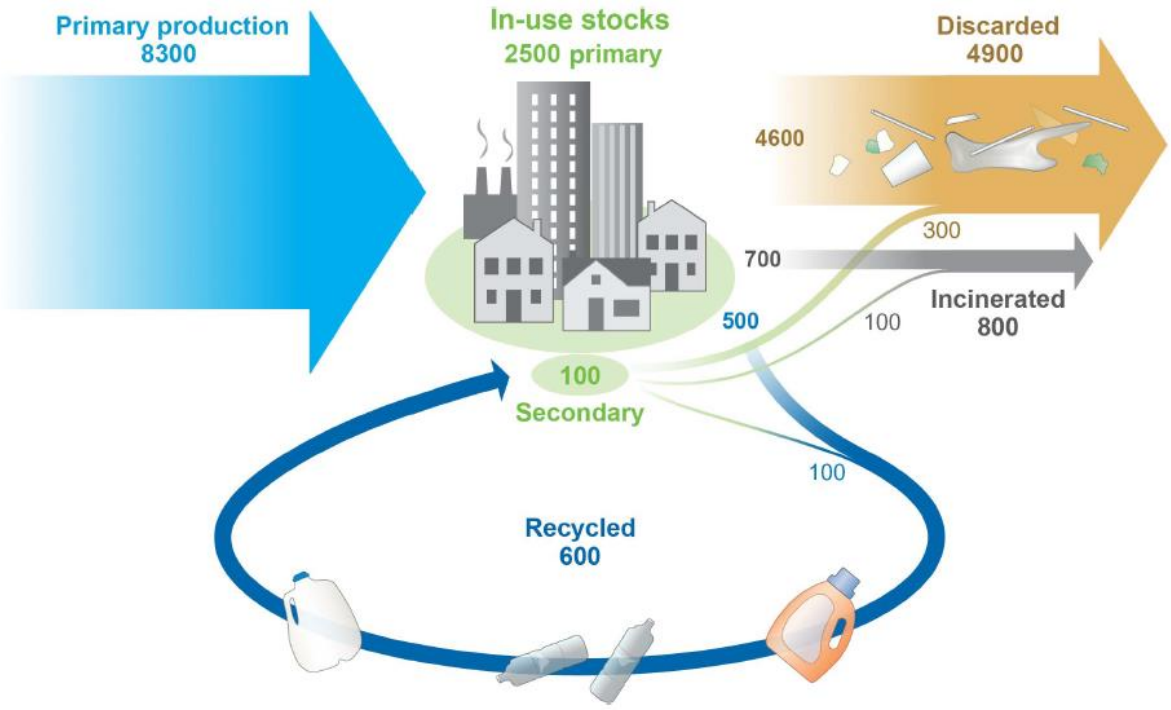

Figure 1: Global production, use, and fate of polymer resins, synthetic fibers, and additives (1950 to 2015; in million metric tons)[3].

4900 Mt of waste plastics have already been discarded globally over a 65-year period, but current trajectories are predicting continued exponential growth of waste plastic generation, which can be seen in Figure 2. Even with moderate advancements in recycling technologies, the amount of discarded waste plastic is predicted to grow substantially over the next 30 years. Thus, it is essential that a revolutionary recycling process gets developed in the near future, as to avoid an overwhelming amount of cumulative plastic waste in the environment.

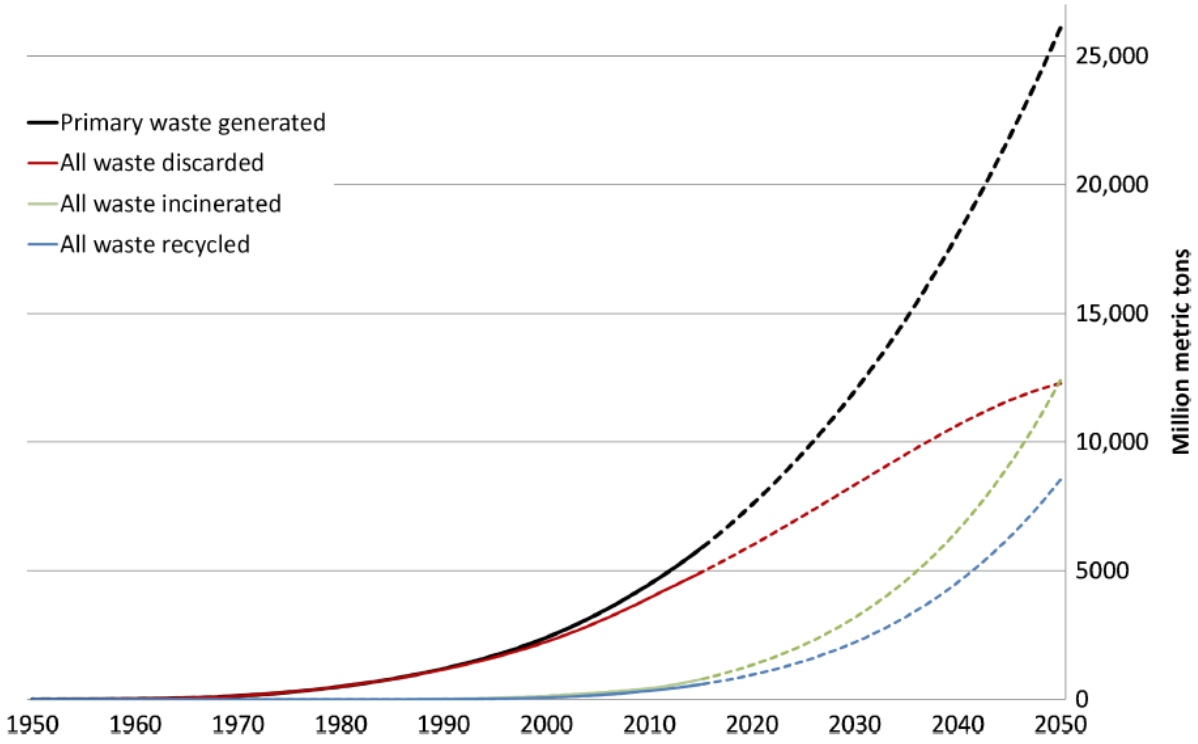

Figure 2: Cumulative plastic waste generation and disposal (in million metric tons)[3].

Of the 8300 Mt of plastic produced globally from 1950 to 2015, 7300 Mt were non-fiber plastics. 36 mass% of all non-fiber plastics produced were high-density polyethylene (HDPE), representing the single-largest individual contributor to that number[3]. Thus, it would be useful to examine the recycling of HDPE waste plastic, which is the ultimate goal of this investigation.

1.2 Polyethylene Properties and Current Recycling Technologies

High density polyethylene is a ubiquitous plastic product, known for its use in water bottles, piping, milk jugs, and many similar products[4]. HDPE is a popular plastic due to its malleability (with a melting point of around 130 ^{o}C), resistance to corrosion, high strength to density ratio, and most importantly for this investigation, a relative ease of recyclability

as compared to other types of plastic. This, alongside its abundance, makes it an attractive option for recycling. However, as of 2018, less than 30% of HDPE bottles in the US were recycled[5]. If a significant value-added recycling process were able to be created for HDPE, that recycling percentage would likely increase.

The theoretical chemical structure of HDPE is $(C_2H_4)_n$, which is potentially a very useful chemical formula for creating a variety of fuel products since it is composed almost entirely of hydrogen and carbon. However, almost all products made from HDPE have a slight amount of contamination from other chemical species, which can make recycling efforts more difficult. A demonstration of these contaminants can be seen in Table 1, which is a proximate and ultimate analysis of waste HDPE via an elemental analyzer; this investigation will focus on the middle column analysis of HDPE.

Table 1: Proximate and ultimate analysis of waste HDPE[6].

Properties	Present study (Waste HDPE)	(HDPE) (Parikh *et al.*, 2009)	(Mixed Plastics) (Kim *et al.*, 2010)
Proximate analysis			
Moisture content	0.00	0.00	1.37
Volatile matter	100	100	92.90
Fixed carbon	0.00	0.00	1.14
Ash content	0.00	0.00	4.59
Ultimate analysis			
Carbon (C)	80.58	84.95	79.9
Hydrogen (H)	13.98	14.30	12.6
Nitrogen (N)	0.60	0.55	-
Sulphur (S)	0.080	-	-
Oxygen (O)/Others	5.19	0.20	5.10
Chlorine			1.13
GCV (Mj/Kg)	45.78	-	44.40

While the contaminants present in HDPE may present a problem for recycling, the proximate analysis reveals results that are promising for potential recycling methods. There is no moisture content, fixed carbon, or ash content present in the HDPE, meaning that all of the plastic can volatilize, which can allow for a recycling process with no unwanted accumulation.

For current recycling methods of HDPE, the first step is the separation from other plastics followed by cleaning, in order to achieve the purest HDPE stream possible. This investigation is focused on the thermochemical processing of HDPE, so these isolation methods will not be examined in-depth. The isolated HDPE then goes through a granulation process and is shredded or melted down into granules or pellets[7]. These slightly contaminated HDPE pellets are then combined and reshaped into a variety of products, including non-food grade bottles, piping, and playground equipment. As can be seen, there are product limitations due to the lowered plastic quality, so different thermochemical routes may be desired for these HDPE pellets to create a product that is more purified and valuable. One possibility of a new recycling product from HDPE that is being studied is synthesis gas, or syngas. The properties of syngas, as well as current HDPE recycling efforts to produce it, will be explored in the following section.

1.3 Syngas and Project Motivation

Syngas is a gaseous compound composed primarily of hydrogen and carbon monoxide, and typically much smaller amounts of carbon dioxide and water. It is commonly found as the gasification product of hydrocarbon feedstocks, such as biomass and carbon-based waste products[8]. It is very versatile and can be used in a wide range of industrial applications, including powering internal combustion engines, being

processed further to create fuel products, powering turbines, and more[9]. The variety of applications for syngas can be seen in Figure 3. Depending on what the ratio of hydrogen to carbon monoxide is in the syngas, it can be used to create different products. For example, with an H_2/CO ratio of around 2, there is a simple pathway from syngas to gasoline production through both Fischer-Tropsch Synthesis and methanol formation.

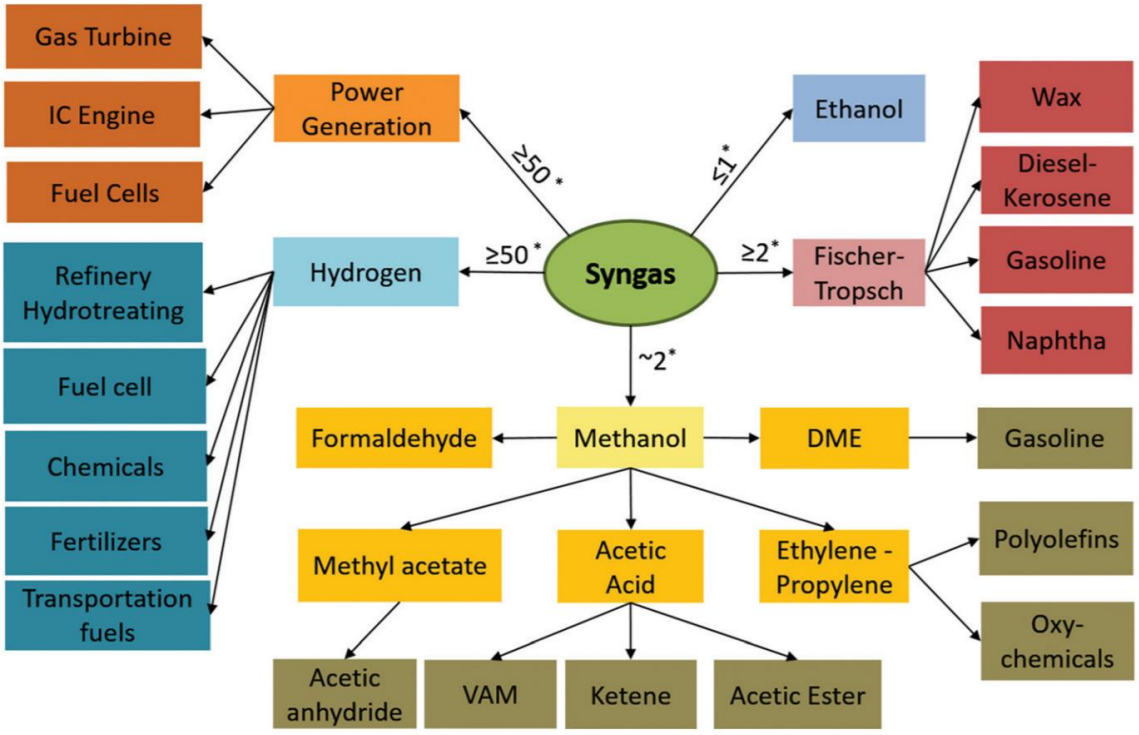

Figure 3: Range of possible syngas derivatives (*H_2/CO molar ratio)[9].

Despite its usefulness as an intermediate product and relatively simple chemical composition, manufactured syngas occupies less than 2% of the world's primary energy consumption. Thus, its production from recycled or sustainable material is worth investigating due to its versatility, market potential, and potentially sustainable production.

Many research groups have already begun looking at recycling waste plastic, specifically HDPE, into syngas. It is an attractive option to use HDPE for syngas to methanol production, since the molar ratio of hydrogen to carbon in waste HDPE is almost exactly 2, which is ideal for creating syngas with a desired H_2/CO ratio of 1 from direct pyrolysis, and can be modified to a specified ratio based on production methods and conditions. It follows that there are a large number of processes to convert polyethylene into the desired hydrogen and carbon monoxide mixture, with the best method still being an active area of research. Efforts toward this include He et al., who developed a method in 2009 that converts waste polyethylene to syngas using a catalytic steam gasification approach in a fixed bed reactor[10]. They utilized a NiO-Al_2O_3 catalyst for this reaction, held the reactor at 900 ^oC and 1 atm, and were able to achieve a syngas purity of over 64 mol%. This reaction created the undesired products of unreactive char, as well as carbon deposition (mainly char), which deactivated the catalyst. This study found that increasing reaction temperature results in a higher conversion of HDPE to syngas, a higher H_2/CO ratio, and a lower yield of char and tar. Their metal oxide catalyst was found to increase hydrogen content and decrease char and tar formation.

A similar study was performed by Saal et al. in 2015, where they performed a pyrolysis-gasification/reforming method on polyethylene to form syngas in a two-stage fixed bed reactor[11]. The first stage involved the pyrolysis of the HDPE, which was performed at 500 ^oC with nitrogen and carbon dioxide injection. The second stage was operated at 800 ^oC with Ni-Mg-Al catalyst and steam injection, and further gasification and reforming reactions took place. From these two steps, they were able to achieve a syngas purity of above 74 mol%. However, this process created unwanted methane from

steam injection, as well as carbon deposition. They found the two-stage setup advantageous over a single stage due to increased hydrogen production as a result of the second stage gasification. They also found that carbon dioxide injection increased both hydrogen and carbon monoxide production, as well as reducing carbon deposition. They found the presence of the metal catalyst increased hydrogen production, similar to the other study. The primary challenge discovered in the conversion of HDPE to syngas is not the production rate or purity of syngas, but the accumulation of undesired side products.

It is clear that waste plastic has become a prominent issue in the modern world, with HDPE being a main contributor. Therefore, this investigation will further examine the conversion of HDPE waste plastic into syngas in order to create a recycling process that can both remove a waste product and create a valuable product used to make fuels. This problem will be examined using chemical looping technology, which functions differently than any of the methods used in the previous described research. The fundamentals of chemical looping will be examined in great depth in the following section, as well as why it is a promising method for HDPE to syngas conversion.

Chapter 2: Principles and Application of Chemical Looping Technology

2.1 Description, Advantages, and Challenges of Chemical Looping

An increasing area of interest in engineering efforts for the environment is chemical looping, which is able to greatly simplify carbon dioxide capture in power plant operations by creating a stream of highly concentrated carbon dioxide as well as water[12]. This is done by a process known as chemical looping combustion, where incoming hydrocarbon feedstocks, such as coal or biomass, are fully oxidized by solid, metal oxide-based compounds known as oxygen carriers, which generally appear in the form of pellets/beads. This process is useful for carbon capture and sequestration, yet not quite as useful for the creation of any valuable products. However, if the incoming carbonaceous feedstock is only partially oxidized rather than fully oxidized, then chemical looping can be used to make mainly carbon monoxide and hydrogen, i.e. the components of syngas, rather than carbon dioxide and water. This process is known as chemical looping partial oxidation, and is achieved by determining an optimal ratio between the flow rate of the feedstock and of the oxygen carrier so that primarily hydrogen and carbon monoxide are produced.

There are two reactors in a chemical looping system, a reducer and a combustor. The naming of these reactors follows the metal oxide oxygen carriers in the system; the

oxygen carrier is reduced (loses lattice oxygen atoms) in the reducer by the carbonaceous feedstock to produce syngas and typically several unwanted species, including water, carbon dioxide, unconverted solid carbon, and more. The solid oxygen carrier is then sent to the oxidizer, where it is regenerated to its oxidized state. This is done by reacting the spent oxygen carrier with the oxygen that occurs naturally in air. The unconverted carbon char deposited in the reducer also flows to the combustor with the oxygen carrier and is converted to carbon dioxide. The air stream is then bled out of the system as depleted air, and the restored oxygen carrier is returned to the reducer to begin the process anew, while the unconverted carbon is removed from the system as carbon dioxide. This comprises the “looping” aspect of the chemical looping process. Both these reactors operate at very high temperatures (typically ≤1000 ^{o}C) in order to volatilize the carbonaceous feedstock and create rapid reaction kinetics. A simplified diagram depicting the chemical looping partial oxidation process can be seen in Figure 4.

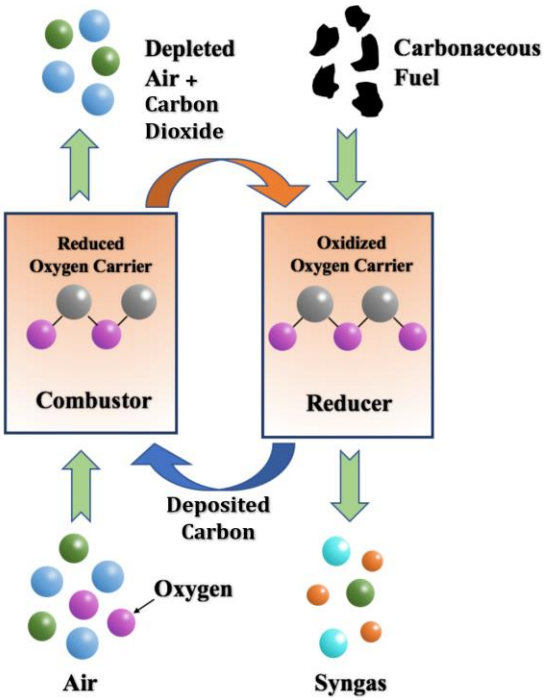

Figure 4: Diagram of chemical looping partial oxidation process[13].

Chemical looping provides many advantages over traditional gasification methods: the solid metal oxides act as intermediate oxygen carriers that allow oxygen to react with a feedstock while not being exposed to any additional gases. This allows for a higher syngas purity with no nitrogen or other atmospheric gases present in the end product. The alternative method would be to oxidize the hydrocarbon fuel with pure oxygen, which is far more expensive than replenishing a reusable oxygen carrier with air. Chemical looping technologies are also able to utilize many species as feedstocks, as long as they are hydrocarbon-based and able to volatilize; this will allow for future chemical looping research on more plastics than just HDPE. With high operating temperatures, larger hydrocarbons are generally cracked more easily, creating less unwanted hydrocarbon byproducts. Since chemical looping is a relatively new process, there are still a number of challenges that must be overcome in its research, such as finding an oxygen carrier with a long lifespan and sufficient reduction-oxidation capabilities. Other challenges include developing effective solids circulation, reducing carbon deposition, converting a higher percentage of hydrocarbons, and creating effective heat recovery systems. Ultimately though, chemical looping has the potential to serve as a process that can convert waste plastic into a valuable fuel product with minimal environmental impact.

2.2 Previous Studies and Planned Application of Chemical Looping

This investigation will focus specifically on the reducer of the chemical looping system, in a co-current, moving bed configuration; the exact specifications of this reactor are detailed in a later section. There have already been other studies performed on this exact type of reactor in the L.-S. Fan Facility for Clean Energy Research at Ohio

State[13,14,15], but they examined the biomass-to-syngas (BTS) process, which employs biomass as a feedstock rather than HDPE. These parallel studies will be examined to determine the behavior of this particular chemical looping reactor system.

The first study by Xu et al. sought to develop an efficient BTS process that can lower the production cost of sustainable, biomass-based liquid fuels and chemicals[14]. The process is able to reduce operating costs due to the creation of a syngas product that is of high enough purity that additional unit operations are not required, such as an air separation unit, a steam reformer, a tar reformer, or a water-gas-shift-reactor. A bench-scale version of the reactor mentioned previously was used for this experiment, and the co-current moving bed reactor setup eliminates any back-mixing, channeling, or bypassing of gas and solid reactants. The oxygen carrier used in this experiment is an iron-titanium composite metal oxide (ITCMO), which can crack the volatile hydrocarbon species produced from biomass pyrolysis, and can also be used to adjust the syngas composition by altering the amount of oxygen carrier flow relative to biomass flow. This oxygen carrier has been proven to provide sustained reactivity over the course of multiple redox reaction cycles in a chemical looping system. This investigation used woody pellets for its biomass, and the biomass and oxygen carrier were mixed at a specified ratio before being charged to the reactor. This ratio was determined by modeling the chemical looping reactor in Aspen Plus simulation software, where the reaction kinetics and thermodynamic data were determined. This simulation also allowed for the determination of the rest of the reactor's operating conditions, with an H_2/CO target ratio of 2, suitable for methanol production. For the experimental reactor runs, the oxygen carrier was initially flowed into the reactor until it reached 1000 ^{o}C, then the biomass was introduced and

flowed until steady state was achieved. This experiment also utilized periodic steam injection in order to elevate the hydrogen gas concentration in the product gas. The results of these experiments very closely resembled the results found from the process simulation. They determined that the ITCMO oxygen carrier used is capable of partially oxidizing the biomass with the production of very few unwanted side products. They also found that the reactor ensures uniform conversion of the oxygen carriers and controls the residence time of both gaseous and solid species well. Overall, they were able to determine that the BTS process is capable of producing a high quality syngas product with the desired H_2/CO ratio, without the requirement of additional unit operations.

The other two investigations were experimentally similar to the previously described investigation, but were able to determine several more useful properties of the reactor. One of the investigations examined woody pellets and corn cob pellets as the biomass feedstock, as well as the effect of biomass feedstock pellet diameter by pulverizing some biomass pellets into much smaller pieces[13]. This study determined that the BTS process in a chemical looping reactor is capable of producing high purity syngas for multiple carbonaceous feedstocks, which demonstrates the potential use of a greater array of feedstocks that are able to produce syngas in this process. They also determined that syngas purity and CO/CO_2 ratios are higher with pellets of larger diameter, whereas H_2/CO ratios are higher with pellets of smaller diameter, likely because the unreacted biomass chars did not have enough residence time for reaction with water and carbon dioxide. The other study performed on the same reactor likewise used woody pellets and corn cob pellets and had similar findings, but it was determined that steam injection into the reactor reduces syngas purity in the product stream[15]. This is caused by the carbon

in the biomass completely oxidizing in order to provide sufficient heat to convert the injected water into steam, as well as the water providing extra oxygen when injected, causing unwanted carbon dioxide production.

All of these studies provide a solid understanding of the behavior of the co-current moving bed reactor, and this allows for further investigation of its capabilities for syngas production. This investigation will specifically focus on this reactor, and will explore the potential of using HDPE as a carbonaceous feedstock rather than biomass.

2.3 Purpose of Investigation

This investigation focuses on the process of chemical looping partial oxidation and its application to HDPE waste plastic to form a high purity syngas product. HDPE is an ideal choice for a potential feedstock for the chemical looping partial oxidation process to syngas, since it is composed primarily of hydrogen and carbon at a molar ratio of two to one. By performing a single step pyrolysis of excess HDPE with forced carbon deposition (to raise the amount of hydrogen available relative to the amount of carbon) in a chemical looping reducer, a syngas product can be formed with an H_2/CO ratio of 2; this product can then be used to form gasoline either by Fischer-Tropsch synthesis or via a methanol intermediate pathway. HDPE was also determined from an elemental analysis to provide 100% volatile matter, and this combined with its relatively low melting point means it should volatilize as thoroughly as required in a chemical looping reactor system. The reactor used for experimentation is the co-current moving bed reducer described in the previous section. The purpose of this experiment is to determine the ideal operating conditions of a chemical looping reactor for the conversion of HDPE to high quality syngas. These operating conditions include the reactor temperature, oxygen carrier flow

rate, and HDPE flow rate, and the determination of these values will be presented in the following section. The overall goal of this investigation is to be able to create a process that can remove the severe environmental threat of waste plastic and use it to produce fuel or other chemical products in a sustainable manner with minimal emissions.

Chapter 3: Process Simulation and Determination of Operating Conditions

3.1 HDPE to Syngas Process Model

A BTS process model was configured in Aspen Plus for use in previous experimentation to determine the behavior of the co-current moving bed reducer[13,14,15]. The simplified flow diagram for the process model can be seen in Figure 5. The process model has been modified to fit the needs of this specific investigation.

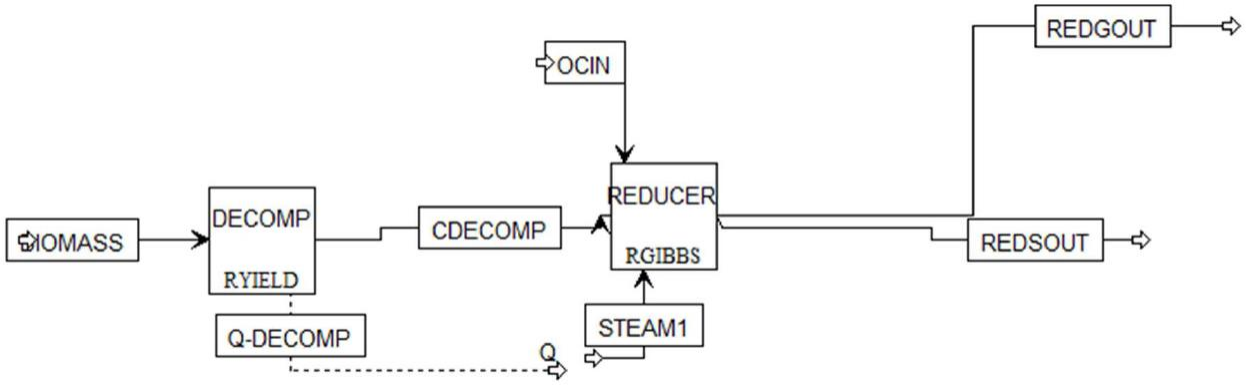

Figure 5: Flow diagram of BTS process model[15].

The process is simulated using a verified performance model that uses the RGibbs method; this model calculates the reactor's gaseous and solid products equilibrium composition[14]. The model assumes that a chemical looping system can perform autothermal operation, which means that no external heat is necessary to keep the system at a high temperature because the system is able to regulate its own temperature

through a series of exothermic reactions. Because of this, the reactor model assumes adiabatic conditions to represent an industrial reactor with no external heating requirements. Autothermal operation is often used primarily to describe processes in which syngas is produced.

The inputs into the original process model include the flow rate of the ITCMO oxygen carrier, biomass flow rate, enhancer gas flow rate, steam flow rate, proximate and ultimate analyses of the biomass, and the reactor operating temperature. Enhancer gas and steam flow rate are not examined in this investigation and are thus set to zero. The biomass flow rate and proximate and ultimate analyses are replaced by those of HDPE for this investigation. With this process model, it is possible to determine the theoretical results of the thermodynamic equilibrium of the HDPE to syngas reaction. From previous use of this process model, the simulation results closely align with the experimental operation of the reactor, and thus the optimal operating conditions for the reactor can be determined before the reactor is operated.

3.2 Operating Conditions Examined and Desired Variable Responses

The primary operating conditions examined in this investigation are the HDPE flow rate, the ITCMO oxygen carrier flow rate, and the operating temperature of the reactor. The temperature is varied to determine its effect on reaction kinetics and the resulting thermodynamic equilibrium. The ratio between the flow rate of HDPE and the flow rate of the oxygen carrier is a more useful individual variable to examine than the separate flow rates; this is because this ratio governs the extent of oxidation of HDPE. A low ratio of

HDPE to oxygen carrier results in more complete oxidation of HDPE, meaning more carbon dioxide is produced relative to the amount of carbon monoxide. This is undesirable, since an ideal syngas mixture is composed of primarily hydrogen and carbon monoxide, with minimal carbon dioxide present. However, if the HDPE is introduced at a high enough ratio compared to the oxygen carrier, the oxygen carrier is starved of its lattice oxygens and forced carbon deposition occurs. This allows the amount of hydrogen produced to be maximized while the amount of carbon monoxide produced is reduced with less available carbon; this can generate a syngas purity with the ideal H_2/CO ratio of 2 with minimal contaminants produced. A useful metric for examining the ideality of the syngas product is through syngas purity, which is a comparison of syngas composition to total gas composition. The calculation of syngas purity used in this investigation can be seen in Equation 1. This calculation assumes that the only other gases present in the product gas are carbon dioxide and water, since the concentration of all other species is relatively low.

Equation 1

$$y_{sg} = \frac{mol\ H_2 + mol\ CO}{mol\ H_2 + mol\ CO + mol\ CO_2 + mol\ H_2O} = \frac{mol\ syngas}{mol\ total} = y_{H_2} + y_{CO}$$

Since syngas is the primary product of this reaction, it makes sense that a high syngas purity is desirable (as close to 1 as possible); however, the syngas purity is only one of several metrics used to determine optimal performance in the process model. More performance metrics include hydrogen and carbon monoxide flow rates and amount of carbon deposition. While total flow rate of hydrogen and carbon monoxide is important since a high flow rate of product is beneficial, the ratio between the two flow rates is just as important, similar to the HDPE to oxygen carrier ratio. As discussed earlier, the H_2/CO

ratio is what determines which product(s) can be synthesized from the syngas product, and the target ratio in this investigation is 2, which is ideal for making methanol and Fischer-Tropsch synthesis. Similarly, the CO/CO_2 ratio is examined, with a high value desired because carbon dioxide often interferes with downstream product formation. Carbon deposition is also an important metric to examine since it is the amount of relatively unreactive solid carbon produced in the reducer that would flow to the combustor reactor and be converted into carbon dioxide. Although forced carbon deposition is required in the reducer to create the ideal syngas product, its value should be as close to zero as possible to minimize the amount of carbon dioxide produced in the process. With the adjustable operating parameters and desired responses determined, optimal operating conditions can now be determined by performing simulations of the process model.

3.3 Sensitivity Analysis and Determination of Operating Conditions

In order to determine which operating conditions should be tested on the moving bed co-current reducer, a sensitivity analysis of the described process model was performed, with varying reactor temperature, HDPE flow rate, and oxygen carrier flow rate. The response variables tested were the flow rates of carbon monoxide, carbon dioxide, hydrogen, and water, as well as H_2/CO ratio, CO/CO_2 ratio, syngas purity, and carbon deposition. The general trends between each of these variables were determined by graphing the sensitivity analysis results against each other for each operating condition and response variable. The result of this can be seen in Table 2, where the trends of the response variables are shown for increasing operating condition values. A positive

response is indicated with a green arrow, a negative response is indicated by a red arrow, and no noticeable effect is denoted by a black dash. This information allows for the determination of optimal operating conditions within the constraints of the performance capabilities of the reactor.

Table 2: General trend results between reactor variables from sensitivity analysis.

With Increasing …	Response Variable	Trend
HDPE Flow Rate	H_2 Flow Rate	↑
	CO Flow Rate	-
	H_2/CO Ratio	↑
	Syngas Purity	↑
	Carbon Deposition	↑
Oxygen Carrier Flow Rate	H2 Flow Rate	-
	CO Flow Rate	↓
	H2/CO Ratio	↓
	Syngas Purity	↓
	Carbon Deposition	↓
HDPE to Oxygen Carrier Ratio	H2 Flow Rate	↑
	CO Flow Rate	↓
	H2/CO Ratio	↑
	Syngas Purity	↑
	Carbon Deposition	↑
Reactor Temperature	H2 Flow Rate	↑
	CO Flow Rate	↑
	H2/CO Ratio	↓
	Syngas Purity	↑
	Carbon Deposition	↓

With the general trends determined, specific values that the reactor can operate at can now be found. The ITCMO oxygen carrier flow rate range tested was from 20 – 25 g/min; the feeder of the system is more inaccurate below 20 g/min, and too far above that

value requires additional fuel feed. The HDPE flow rate was varied from 5 – 6 g/min, which corresponded to the amount of oxygen carrier needed to create a syngas H_2/CO ratio near 2 at thermodynamic equilibrium with forced char formation. The temperature of the reactor was typically around 1000 ^oC in previous studies; that value should not be exceeded by too much due to reactor safety constraints, and too far below that value creates unfavorable reaction kinetics, so the temperature range tested was from 900 – 1000 ^oC.

With all of these conditions being varied simultaneously, several of the most appealing sets of conditions were extracted based on their response variable values. Since all flow rates of individual exit gas species were similar, the primary values considered for optimization were H_2/CO ratio, CO/CO_2 ratio, syngas purity, and carbon deposition. Calculations were performed that equally weighted those three values, with the best value achieved for an individual response variable being the weighting factor (i.e. if the highest syngas purity was 99.8%, then a 99.5% purity would be considered 99.5 / 99.8 x 100% = 99.7% of optimal performance). With these three performance criteria factored together, the top performing set of reactor conditions was determined, and can be seen in Table 3.

Table 3: Optimal reactor operating conditions determined from process model sensitivity analysis.

Operating Conditions			
HDPE Flow Rate	Oxygen Carrier Flow Rate	HDPE/OC Mass Ratio	Operating Temperature
5.6 g/min	21 g/min	0.267	1000 ^{o}C
Response Variables			
CO Flow Rate	H_2 Flow Rate	CO_2 Flow Rate	H_2O Flow Rate
5.47 g/min	0.788 g/min	0.0204 g/min	0.0282 g/min
H_2/CO Ratio	CO/CO_2 Ratio	Syngas Purity	Carbon Deposition
2.00	421.4	99.65%	2.38 g/min

This set of reactor operating conditions is what is tested on the moving bed co-current reducer in this investigation. The reactor has proven in past studies to be capable of fulfilling these prescribed operating conditions, and a more thorough description of the reactor, materials, and other utilized equipment will be given in the following section.

Chapter 4: Chemical Looping Reducer Setup

4.1 Materials and Equipment

This investigation will focus on the use of a 10 kWth moving bed co-current reducer that has been studied previously, and represents the reducer in a chemical looping reactor system[13,14,15]. A diagram of the reducer can be seen in Figure 6. An image of the actual reactor setup can be seen in Figure 12, located in the Appendix.

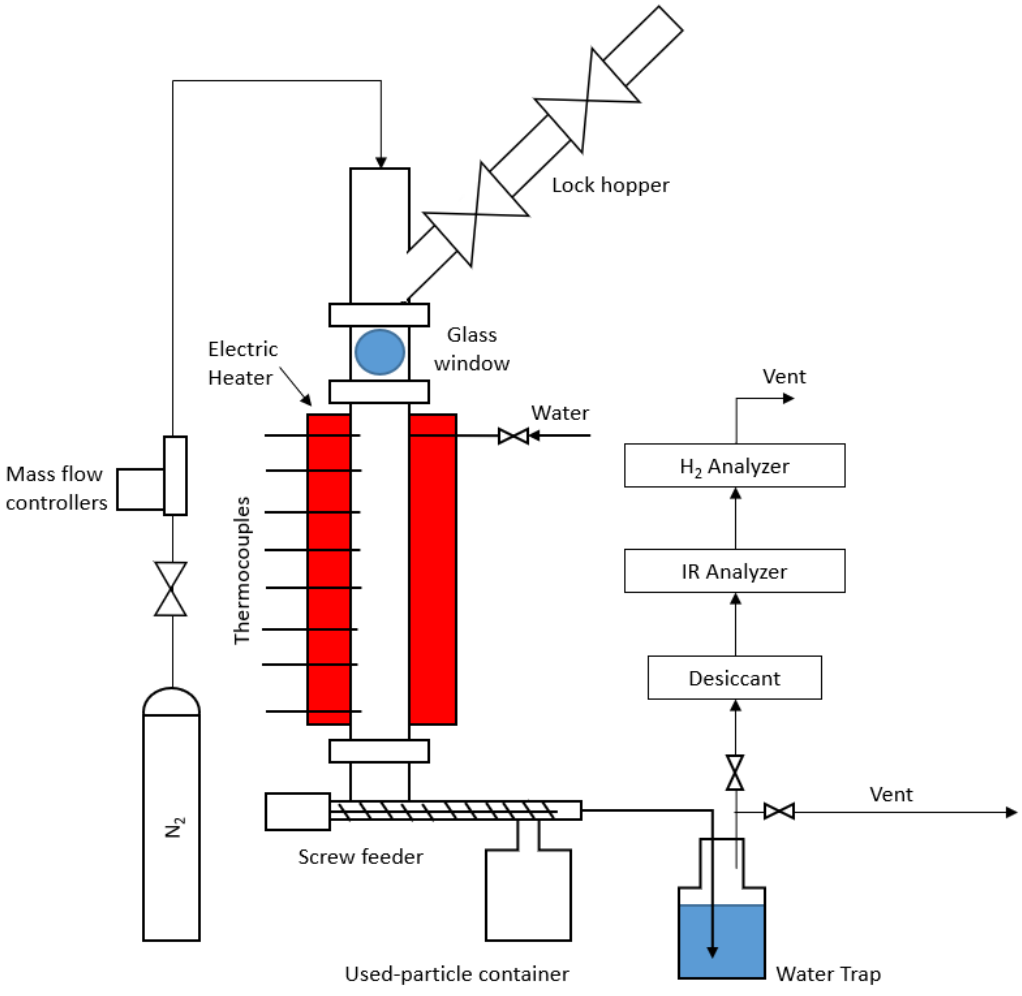

Figure 6: Diagram of co-current moving bed reducer[14].

The solid particles (oxygen carrier and carbonaceous fuel) are loaded into a lock hopper at the top of the reactor, which is closed off to the atmosphere after solids are added, similar to a full chemical looping system. The gas-solid partial oxidation reaction takes place in a 1.5 - inch inner diameter by 100 cm length stainless steel tube, and a screw feeder located at the bottom of the reactor ensures a constant discharge rate of any remaining species in the solid phase. The screw feeder is controlled by a DC controller with a linear relationship between voltage provided and flow rate. The solid oxygen carrier and the deposited carbon char flow from the screw feeder to the used-particle container; there are no solids recirculated in this reactor since it is only modelling the chemical looping reducer. There is a small amount of nitrogen gas flowed to the reactor to flush the lock hopper section of any combustible gases, and it also acts as a tracer gas. The volumetric flow rate of the nitrogen is controlled by a mass flow controller. There are other gas lines connected to the reactor, such as carbon monoxide, carbon dioxide, and methane, that are used to calibrate the gas analyzers. There are two gas analyzers at the end of the reactor to analyze the product gas; one is an infrared analyzer that is used to detect oxygen, carbon monoxide, carbon dioxide, and methane, and the other is a thermal conductivity detector that determines the content of hydrogen gas. Before the product gases are flowed to the analyzers, they go through a water trap and desiccant bed to remove any steam or ash, which would interfere with the analyzer readings.

The reactor itself is kept at a high constant temperature by vacuum-formed semi-cylindrical heating elements lining the outside of the reducer. The temperature of the reaction vessel is tracked by eight type-K thermocouples, and the average of their

readings is used to determine the overall reactor temperature. The glass window at the top of the system is used to determine if the solid mass has passed through the reactor, and if more solid needs to be added to continue steady state operation. The two types of solid particles used in this investigation are the ITCMO metal oxide and HDPE pellets. The oxygen carrier is the same iron-titanium composite metal oxide particle as the one used in the previously described studies, and the plastic particles are composed of 20-melt natural HDPE. Images of all described equipment and the HDPE particles can be seen in Figures 13-19, located in the Appendix.

4.2 Operation of Chemical Looping Reducer

To ensure gas and solid flow accuracy, the screw feeder and gas analyzers must be calibrated; these calibrations are typically performed the day before the experimental reactor run. The screw feeder is calibrated by flowing oxygen carrier particles through the reactor at a specified voltage, measuring the amount of oxygen carrier accumulated in three minutes to determine flow rate, and adjusting the voltage provided to the DC motor until it reaches the desired flow rate (in this case 21 g/min oxygen carrier). The gas analyzers are calibrated by flowing known amounts of oxygen, carbon monoxide, carbon dioxide, methane, and hydrogen one at a time mixed with a known flow rate of nitrogen, then finding the conversion factor to convert the value the analyzer returns to a value of gaseous mol percent.

To begin operation, the heating elements are turned on to get the reactor up to its operating temperature of 1000 ^{o}C. Once the reactor reaches the operating temperature of 1000^{o}C, the HDPE and oxygen carrier particles are mixed together at the specified mass ratio of 0.267 HDPE:OC. This solids mixture is charged to the reactor 400 g at a

time every 20 min to ensure a steady, continuous flow of solids. During the initial phase of adding HDPE, the system has not yet reached steady state, and the reactor tends to oxidize the volatilized HDPE to a greater extent, creating more undesired carbon dioxide than carbon monoxide. After about an hour of adding HDPE, the reactor tends towards steady state, and the reactor reaches its thermodynamic equilibrium and creates more carbon monoxide than carbon dioxide to produce a higher purity syngas with the desired H_2/CO ratio. The mole fractions of the exit gas mixture are measured by the gas analyzers and recorded by a connected computer. After steady state operation has persisted for long enough to collect all the required data, the screw feeder motor and heating elements are turned off in order to cool down the reactor. Nitrogen continues to be flowed to the system in order to reduce any more oxygen carrier reactions. With the raw data for the product gaseous species determined, the performance level of the bench-scale chemical looping reducer can be determined.

4.3 Performance Metrics

The performance of the moving bed reducer must be analyzed primarily using data about gaseous flows, since that is what is recorded in this system. The first performance metric examined is the H_2/CO ratio of the syngas product, which has been discussed previously as being able to determine what product the syngas can be converted into. The calculation of this ratio can be seen in Equation 2.

Equation 2

$$H_2{:}\,CO = \frac{y_{H_2}}{y_{CO}}$$

Similarly, the ratio between carbon monoxide and carbon dioxide is an important value, since it is also important in determining which products can be formed from the syngas. Generally, a high CO/CO_2 ratio is desired since high carbon dioxide content makes product synthesis more difficult. The calculation for this metric can be seen in Equation 3.

Equation 3

$$CO{:}CO_2 = \frac{y_{CO}}{y_{CO_2}}$$

The next performance matrix is syngas purity, which determines what percent of the exit gas is useful product. This value should be as close to 100% as possible, which would require less downstream separation processes to isolate the syngas product. The calculation for this metric had to be altered slightly from the syngas purity calculation defined for the process model, since water is removed by the desiccant bed and there is no water analyzer; this calculation can be seen in Equation 4.

Equation 4

$$Syngas\ Purity = \frac{y_{H_2}+y_{CO}}{y_{H_2}+y_{CO}+y_{CO_2}+y_{CH_4}}$$

The last metric examined for the operation of the reducer is the HDPE conversion efficiency, which is the ratio of the carbon converted from HDPE into gaseous carbon species to the carbon in the carbonaceous fuel. This value determines how efficiently the feedstock is utilized, and how much potential waste is being produced from this process. This calculation requires mass and volumetric flow rate information for each gaseous species, and these values can be found relative to the amount of nitrogen flowing through

the system, since it acts as a tracer gas with a known flow rate. The calculations required to determine HDPE conversion efficiency can be seen in Equations 5-7.

Equation 5

$$V_i\ (Volumetric\ Flow\ Rate\ of\ Species\ i) = \frac{y_i}{(1 - y_{H_2} - y_{CO} - y_{CO_2} - y_{CH_4})} * V_{N_2}$$

Equation 6

$$F_i\ (Molar\ Flow\ Rate\ of\ Species\ i) = \frac{PV_i}{RT}, where\ P = 1\ atm$$

Equation 7

$$HDPE\ Conversion\ Efficiency = \frac{F_{CO,out} + F_{CO_2,out} + F_{CH_4,out}}{F_{SC,in}} * 100\%$$

$F_{SC,in}$ is the moles of solid carbon contained in the HDPE before it is charged to the reactor, determined based on HDPE flow rate and its ultimate analysis. Since all measured gaseous species contain only one carbon per molecule, the sum of their respective moles of carbon can be compared to the amount of carbon in the feed HDPE to determine its conversion efficiency. With these performance metrics determined, the feasibility of HDPE to syngas can now be determined once the necessary data is collected from an experimental reactor run.

Chapter 5: Experimental Results and Discussion

5.1 Raw Data and Observations

To begin the experimental run, the reactor was heated to a value of around 1000 ^{o}C while the screw feeder and gas analyzers were calibrated with oxygen carrier flowing through the system. It took approximately one hour for the reactor to reach its operating temperature, and the average temperature of the reactor throughout the run can be seen in Figure 7. The value appears to be less than 1000 ^{o}C from this graph, but this is due to the thermocouples placed at the extreme ends of the reactor being at a temperature below 1000 ^{o}C, whereas the more central thermocouples were reading values near 1000 ^{o}C.

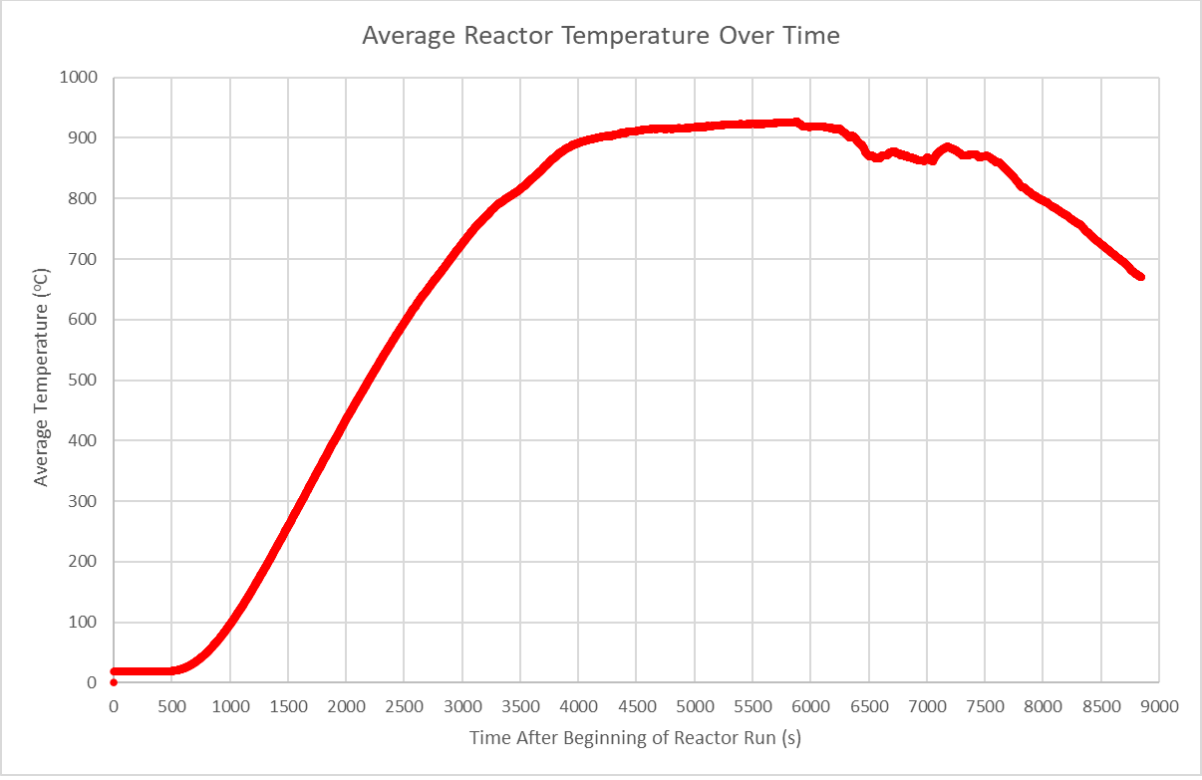

Figure 7: Average temperature of reducer throughout experimental run.

After the reactor reached its operating temperature, the HDPE particles were mixed into the oxygen carrier particles, and shortly after the HDPE began volatilizing and getting oxidized by the oxygen carrier particles. At this point, the reactor began producing the syngas alongside the expected contaminants; the gas profile throughout the reactor operation can be seen in Figure 8.

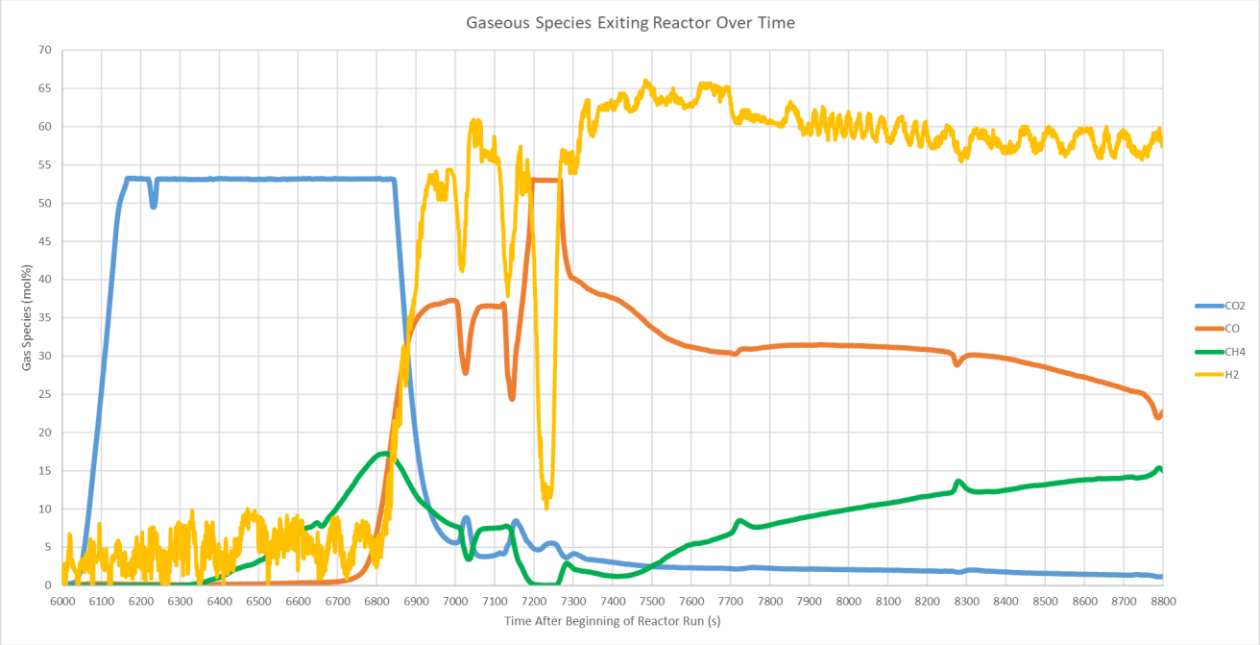

Figure 8: Gas profile of reactor exit gas throughout experimental run.

Due to the nature of the hydrogen analyzer, hydrogen readings experienced quite a bit of noise from water and hydrocarbon interference; this noise was filtered by applying a moving average trendline. From around 6000 – 6900 seconds after operation began, the oxygen carrier was fully oxidizing the volatilized HDPE into carbon dioxide, causing a fairly homogenous gas profile of undesired carbon dioxide. As more volatile hydrocarbons began getting produced relative to the amount of oxygen carrier in the reactor, the lattice oxygens of the oxygen carriers became depleted. This was where the production of

carbon dioxide and water shifted to the partial oxidation products of carbon monoxide and hydrogen, i.e. syngas. This transition from complete to partial oxidation took place from around 6900 – 7600 seconds after the run began. After this time, the reducer entered a state of thermodynamic equilibrium, where relatively steady state values were achieved until around 8400 seconds after the run began.

At around 7500 seconds after reactor operation began, the pressure inside the reactor began rising above atmospheric values, so the heating elements of the reactor were shut off and some of the gas in the reactor were bled off in order to keep the reactor at a safe operating pressure. This pressure buildup likely occurred from improper flow of the deposited carbon char from the HDPE in the form of melted plastic rather than volatilized species. The liquid plastic likely flowed between the solid oxygen carrier particles, sealing off the gas from exiting the reactor fully, causing the buildup of gas and thus pressure in the reactor. This theory is supported by the fact that the mol% of methane began increasing at around this time, which was likely caused by the produced hydrogen gas reacting with the deposited carbon that remained in the reactor bed. This, combined with the decreasing reactor temperature, caused an increase in methane production since it is less likely to be cracked into carbon monoxide at lower temperatures. After the heating elements were turned off, some relatively steady state flow was achieved, but came to a stop when the temperature became too low for the syngas reaction equilibrium to be favorable.

Multiple reactor runs were meant to take place, but due to Covid-19 restrictions as well as gas analyzer availability, only one experimental run was possible in the given timeframe.

5.2 Data Analysis

Since the reducer was operating near steady state values from around 7600 – 8400 seconds after the experimental run began, this is the time span that will be examined for the performance metrics of the moving bed reducer. The first, and perhaps most important performance metric is the H_2/CO ratio, which indicates what products can be made from the syngas. This ratio during steady state reactor operation can be seen in Figure 9.

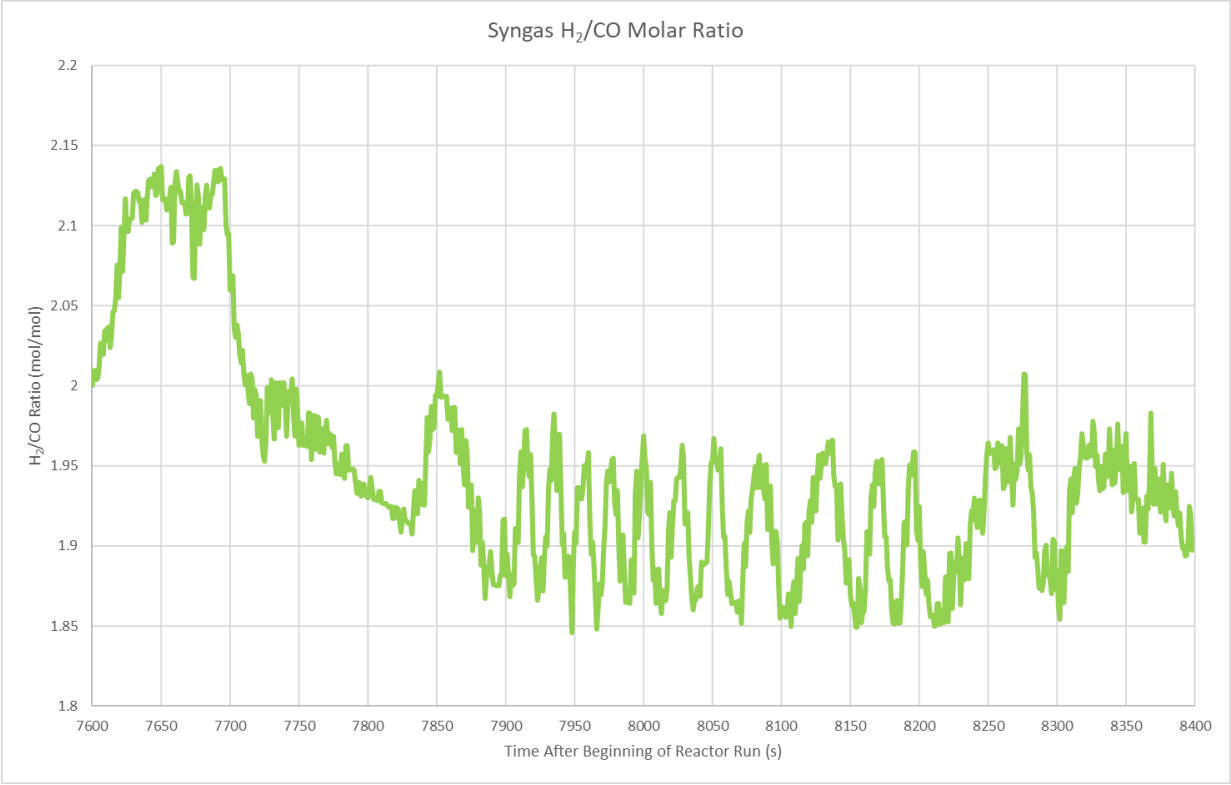

Figure 9: H_2/CO ratio in reactor exit gas during steady state operation.

Ignoring the noise caused by the hydrogen analyzer, the H_2/CO ratio varied from around 1.9 – 1.95 throughout the steady state operation, which is rather close to the

desired ratio of 2 for methanol production. The value from the Aspen Plus simulation was 2.00, so an average steady state value of above 1.9 H_2/CO is less than 5% away from the predicted value, which is still a great value for the downstream synthesis of gasoline from syngas.

The next metric looked at is the CO/CO_2 ratio, which is useful in assessing if there will be two much contaminating carbon dioxide in the syngas product for it to be immediately available for further reactions, and if further separation processes would be needed downstream. The ratio achieved during steady state reducer operation can be seen in Figure *10*.

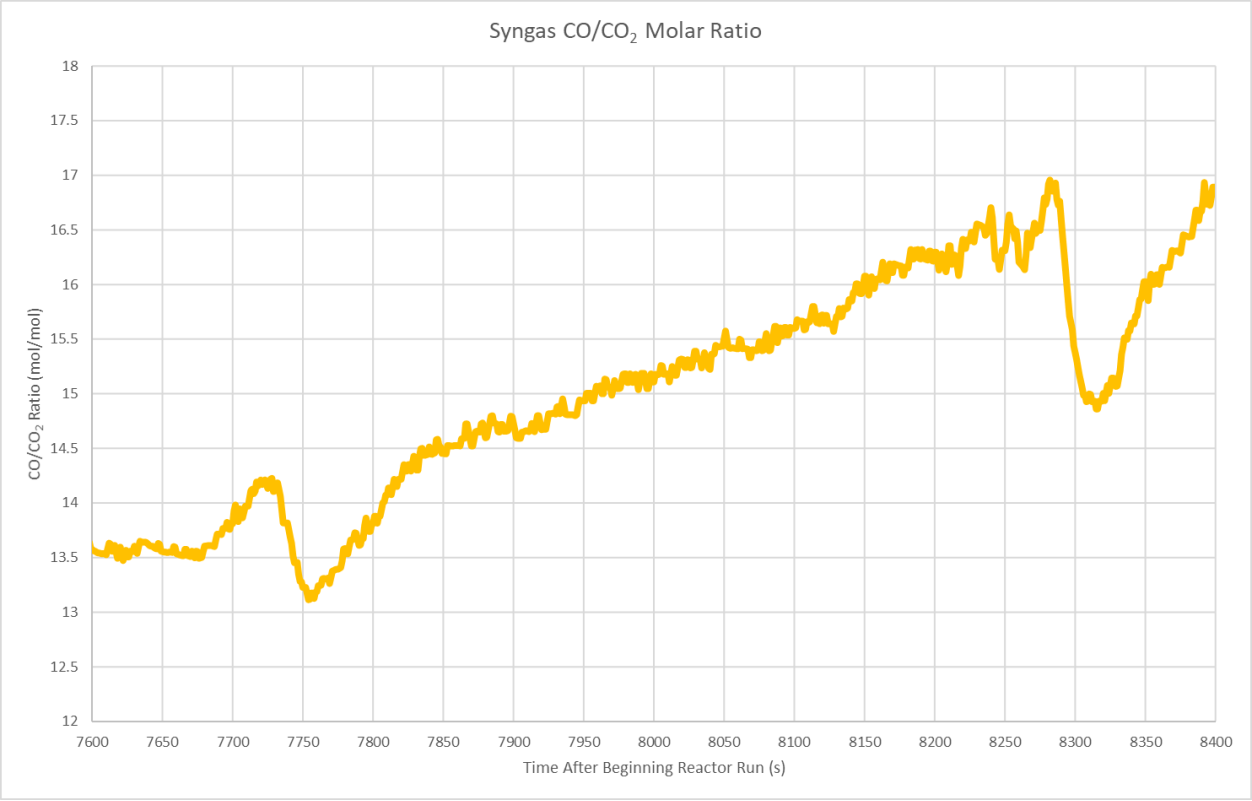

Figure 10: CO/CO_2 ratio in reactor exit gas during steady state operation.

The CO/CO_2 ratio achieved during steady state operation stayed around 15.5, which is drastically different from the value of 421.4 predicted by the process simulation. This is because the oxygen carrier still fully oxidizes a small fraction of the volatilized HDPE into carbon dioxide due to imperfect mixing in the reactor, whereas the simulation assumes perfect mixing and displays a near-zero value of carbon dioxide flow. Although carbon monoxide composition remains relatively stable during steady state operation, carbon dioxide flow is decreasing due to decreasing reaction temperature, which is unfavorable for complete oxidation of HDPE. This is the reason the CO/CO_2 ratio rises slightly during the semi-steady state operation. Although not as ideal as the simulation predicts, having approximately 15 times as much carbon monoxide as carbon dioxide is still promising for creating a usable syngas product.

The last calculated value from the experimental data is the syngas purity, which similarly determines how much further processing the syngas product would need in order to be a useful intermediate product. This metric is calculated with all available gaseous species and assumes that both water and hydrocarbon content in the analyzed gas is low. The syngas purity over time during steady state operation can be seen in Figure 11.

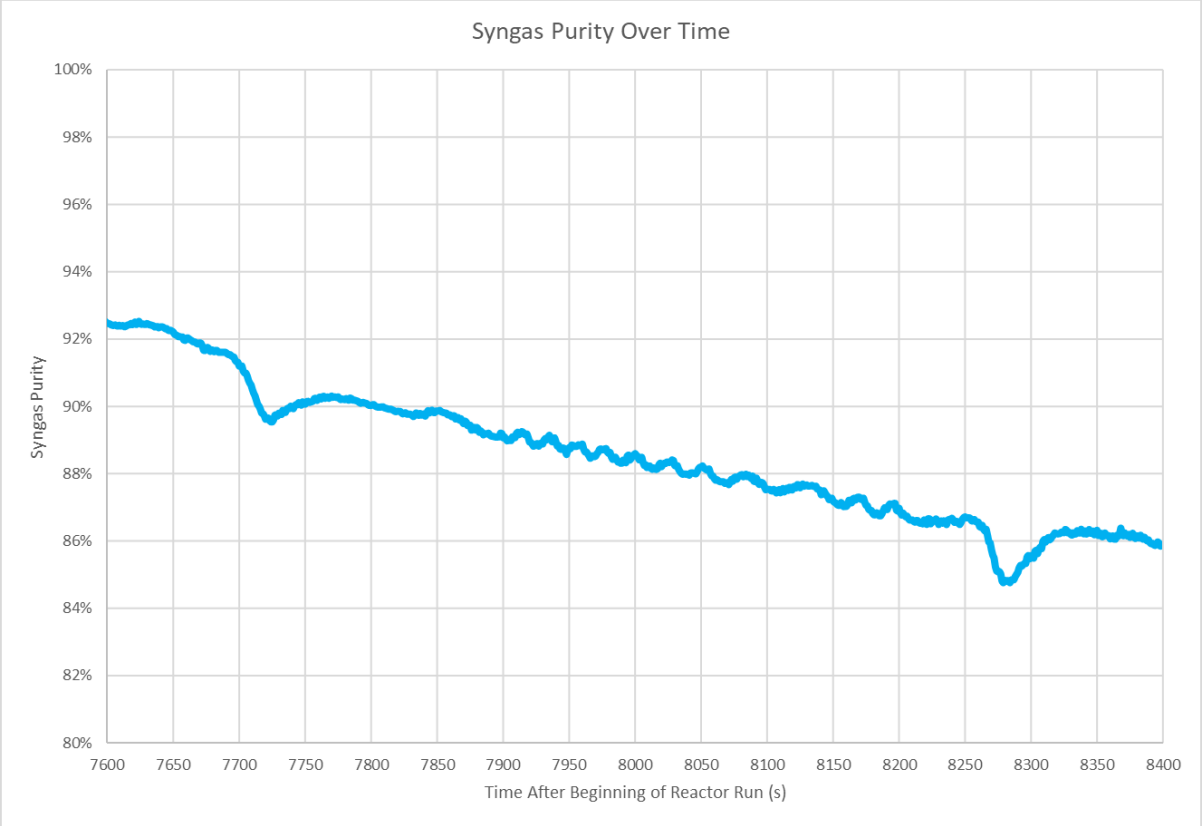

Figure 11: Syngas purity in reactor exit gas during steady state operation.

Syngas purity gradually decreased from around 92% to 86% throughout the course of the relatively steady state operation due to the increasing methane concentration that was a result of decreasing temperature. While this is much lower than the 99.65% purity predicted by the process simulation, it was still a high purity value that began to decrease because of reactor limitations. Achieving around a 90% syngas purity while experiencing reactor difficulties is promising, and a value much closer to 100% syngas purity is likely to be achieved with more optimized reactor conditions and a modified reactor setup that prevents pressure buildup.

Originally, biomass conversion was also supposed to be calculated for steady state operation, but difficulties with gas analyzer readings prevented that from being possible. Regardless, calculated data was obtained that demonstrates the viability of utilizing HDPE as a carbonaceous feedstock in a chemical looping partial oxidation process to form syngas. Additionally, the process model was generally accurate for the reactor run, even with the occurrence of unexpected disturbances.

5.3 Experimental Successes and Challenges

Although the experimental results did not exactly align with the process simulation results, all examined performance criteria displayed promising values for the first attempt at converting HDPE to syngas via a single step pyrolysis process with forced char formation in a chemical looping reducer. The H_2/CO ratio achieved was around 1.9, which was close to the desired value of 2, and can be adjusted simply by altering the feed ratio between HDPE and the oxygen carrier, as well as potentially increasing the amount of carbon deposition to lower the relative amount of carbon monoxide generated. The CO/CO_2 ratio was relatively far away from the simulation value, but could be increased through a more even distribution of incoming solids via mixing in the reactor. Syngas purity was relatively high, even with pressure buildup in the reactor and a shifting of the thermodynamic equilibrium, indicating that the purity would be even higher under more optimal reactor conditions. Obviously, challenges presented themselves during the reactor run, which resulted in an undesired pressure buildup in the reactor due likely to liquid-plastic carbon deposition. This required the reactor heating elements to be turned off, which affected the reactor performance metrics by shifting the reaction equilibrium away from the desired products. One potential solution to this issue is to volatilize the

HDPE particles outside of the reducer to ensure that no melted plastic flows through the reactor, and this could possibly be achieved by utilizing the heat generated from the exothermic reactions in the combustor reactor. Another issue was the noise present in the hydrogen exit gas readings that was likely caused by interference. This issue could be fixed by upgrading the analysis equipment or further processing any remaining hydrocarbons before the gas flows through the analyzer. Besides these two main issues, the reaction proceeded with relatively few hindrances, and provided great insight towards the potential of using chemical looping to form syngas from waste plastic.

Chapter 6: Conclusions and Future Work

6.1 Conclusions

This investigation explored the feasibility of converting HDPE waste plastic into a syngas product that is used as an intermediate product for a wide range of fuels and other chemicals. An analysis of the current global waste plastic issue, the properties of HDPE, and the principles of chemical looping were explored and combined to rationalize the need to recycle waste plastic with chemical looping processes. A previously used process model of a bench-scale, co-current, moving bed reactor was modified to analyze HDPE as a carbonaceous feedstock. The simulation results were promising for an experimental run, and a set of optimized reactor conditions was taken from the simulation for use in a real-world chemical looping reducer. The experimental run gave promising results, with steady state performance metrics of over 90% syngas purity, over 1.9 H_2/CO ratio, and a CO/CO_2 ratio of over 15. These values are very positive for a syngas production process, and indicate that a path from waste plastic to syngas is possible using a chemical looping reactor without the need for any additional unit operations to achieve a high purity syngas product. If proven to be able to scale-up to an industrial level through further testing, this HDPE to syngas process could reduce a major source of pollution while creating a valuable product with minimal environmental emissions.

6.2 Future Work

While this investigation returned useful results for the HDPE to syngas process in a chemical looping reducer, there is much more to figure out with the process before it can be implemented at an industrial scale. First and foremost, getting rid of liquid-plastic carbon deposition is a top priority, and the cause of this could be determined by HDPE volatilization trials, and observing what conditions may cause the plastic to melt rather than volatilize or deposit solid carbon. Additionally, a modification to the reducer system could be made where the HDPE is volatilized separately, then the gaseous hydrocarbon species flow to the reactor without the potential of melted plastic flow. The deposited carbon from this separate volatilization could then be introduced directly to the combustor, so that there would be no potential for reducer pressurization. Additionally, HDPE would likely not need to be brought to 1000 ^{o}C to volatilize in this process, since it has a relatively low melting and boiling point; this could save on energy use and operating cost, especially if heat from the combustor could be used for the volatilization. To determine if the current setup is feasible for scale-up with minimal modifications, more reliable gas analysis would be required, as well as the testing of different sets of operating conditions that limited any carbon deposition.

The HDPE to syngas process could also be tested with steam injection, which would increase the amount of hydrogen present in the system to raise the H_2/CO ratio of the product syngas, since the ratio value of 2 was only possible in this experiment due to forced carbon deposition. This would also introduce more oxygen into the system, which could potentially lower the required amount of oxygen carrier needed. Different forms of waste plastic, such as polypropylene or polyethylene terephthalate, could also be tested

as a carbonaceous feedstock rather than HDPE to determine if they are more feasible options, with different chemical structures and properties than HDPE. Overall, this investigation presents an exciting new direction for plastic recycling technology, utilizing a relatively simple reaction process with a carbonaceous feedstock that is plentiful worldwide.

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Appendix: Reactor, Equipment, and Material Images

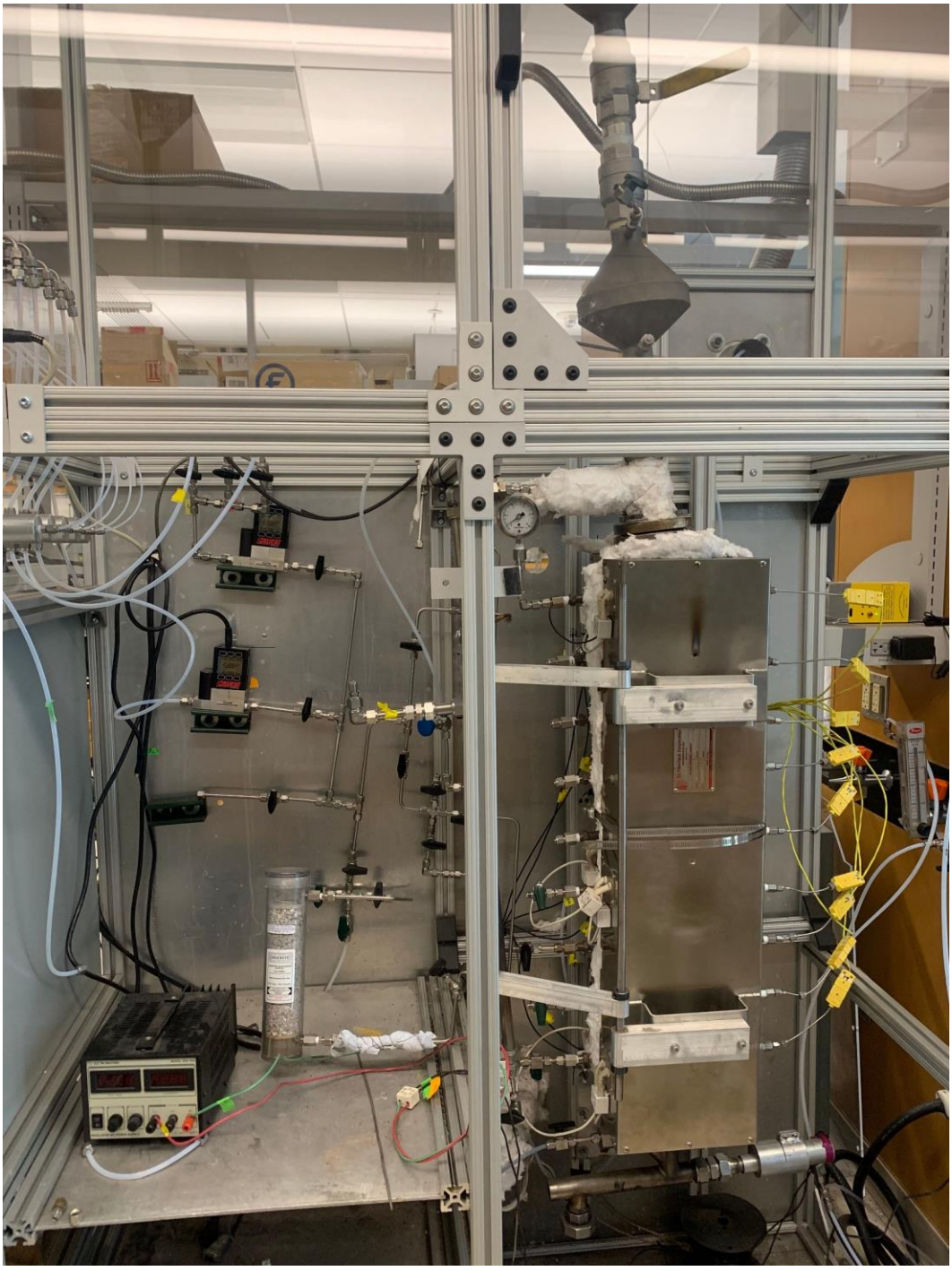

Figure 12: Bench-scale, co-current, moving bed chemical looping reducer

Figure 13: Reactor lock hopper

Figure 14: Reactor glass window to track solid particle flow

Figure 15: Reactor gas lines

Figure 16: Reactor desiccant bed

Figure 17: Screw feeder and solids waste container

Figure 18: Screw feeder DC controller

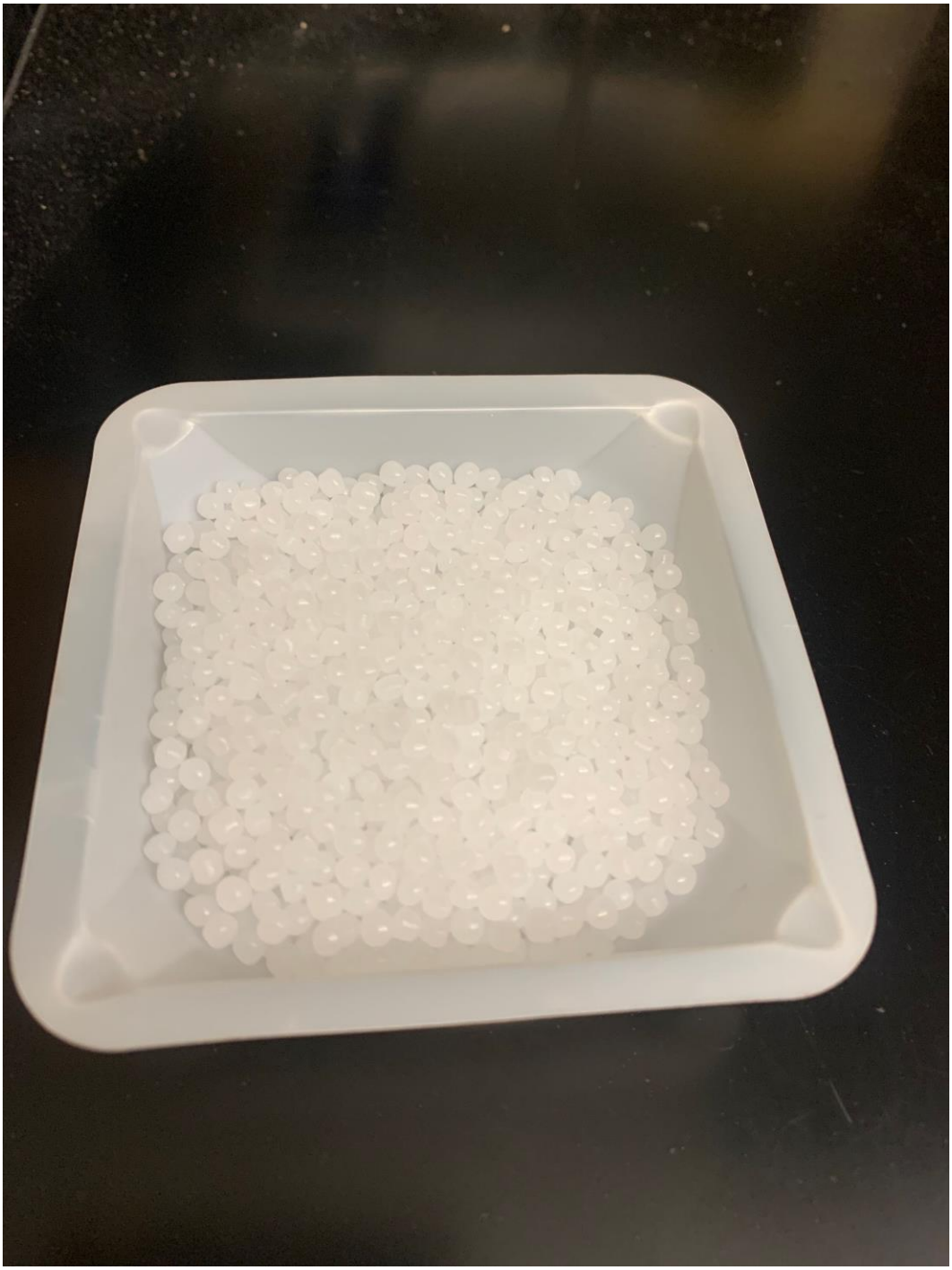

Figure 19: HDPE particles